composition by radicals from the peroxide in spite of the absence of induced decomposition in acetic acid.[13] Thus, the three-halves-order induced decomposition step is more consistent with the present state of our knowledge about the decomposition of acetyl peroxide in carbon tetrachloride.

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(13) The absence of induced decomposition in acetic acid may be due to the ineffectiveness of radicals from the peroxide in inducing the decomposition of acetyl peroxide, or, alternatively, the radicals from the peroxide may react very rapidly with acetic acid to form other radicals which do not induce the decomposition.

NORTH ADAMS, MASS. RECEIVED SEPTEMBER 25, 1950

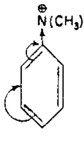
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Electrical Effect of the Trimethylammonium [$-N(CH_3)_3^{\oplus}$] Group

BY JOHN D. ROBERTS, ROBERT A. CLEMENT AND JOHN J. DRYSDALE

A study has been made of the reactivities of a series of anilines and benzoic acids substituted in the meta- and para-positions with trimethylammonium [$-N(CH_3)_3^{\oplus}$] groups. The experimental results offer no support for preferential relay of the inductive effect of a substituent group to the ortho- and para-positions of a benzene ring as postulated by Robinson, Ingold and others. The strong meta-orienting influence of the $-N(CH_3)_3^{\oplus}$ in electrophilic aromatic substitution reactions seems best accounted for by the approach of Pfeiffer and Wizinger.

One of the features of the English electronic theory is the postulation of a preferential relay of the inductive effect of a substituent group to the ortho- and para-positions of the benzene ring. This effect seems to have been evoked originally to explain the very strong meta-orienting influence of the $-N(CH_3)_3^{\oplus}$ group in electrophilic aromatic substitution reactions[1] and has been given some justification by quantum-mechanical calculations.[2] The customary English designation of the electrical influence of the $-\overset{\oplus}{N}(CH_3)_3$ group is represented by I while the counterpart in the resonance interpretation is obtained by consideration of resonance structures such as II. Regardless of symbolism, the effect is presumed to result with induction by the trimethylammonium group of centers of higher positive charge at the ortho- and para-positions than at the meta-positions. In the present investigation, the reactivities of some meta- and para-$N(CH_3)_3^{\oplus}$-substituted benzoic acids and anilines were determined since little experimental evidence for the postulated charge distribution has been obtained except for the strong meta-directing influence of $-NH_3^{\oplus}$ and $-N(CH_3)_3^{\oplus}$ groups.



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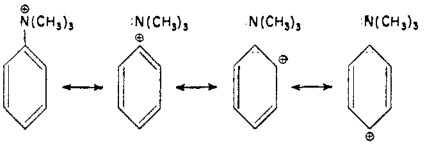
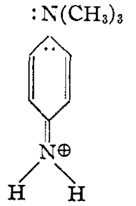
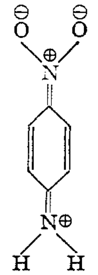


II

The reactions and procedures have been described previously in detail.[3] The experimental results and corresponding σ-constants[4] for the $-N(CH_3)_3^{\oplus}$ group are summarized in Table I. The σ-constants show somewhat larger variations, particularly for the meta-position, than are ordinarily observed.[4] However, the fact that $\sigma_{\text{meta}} - \sigma_{\text{para}}$ is roughly constant from reaction to reaction makes it likely that the variations are due to solvation effects or the like which alter the influence of the meta- and para-substituents on the reactive center to about the same degree. Solvation effects can reasonably be expected to be quite important when the reactions being compared involve entities ranging from dipolar ions to doubly-charged positive ions. Irrespective of the absolute values of the σ-constants of the $-N(CH_3)_3^{\oplus}$ group, there can be no question that the $\sigma_{\text{meta}} - \sigma_{\text{para}}$ figures offer no support for the charge distribution previously postulated.[1,2] Indeed, the $-N(CH_3)_3^{\oplus}$ group seems to have a considerably greater electron-attracting influence at the meta-position than at the para-position. This fact alone does not rule out a powerful "alternating" inductive effect[1] since such an effect could be masked by a more powerful direct coulombic influence. However, the relatively small difference in $\sigma_{\text{meta}} - \sigma_{\text{para}}$ for reactivities of benzoic acids and anilines appears to rule out the possibility that resonance interactions of type III are important in *p*-aminophenyltrimethylammonium compounds in the manner that forms such as IV are important in *p*-nitroaniline and similar compounds.[3b] This conclusion is in agreement with an earlier suggestion[3b] that resonance similar to III is not significant for the trifluoromethyl ($-CF_3$) group. The unimportance of III strongly implies that resonance such as II is likewise unimportant since it is difficult to believe that II could contribute significantly and not lead to III when a *p*-amino group is present



III



IV

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(1) (a) J. Allan, A. E. Oxford, R. Robinson and J. C. Smith, *J. Chem. Soc.*, 401 (1926); (b) C. K. Ingold *Chem. Revs.*, **15**, 225 (1934); (c) *cf.* A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1949, p. 71.

(2) (a) E. Hückel, *Z. Physik*, **72**, 310 (1931); (b) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

(3) (a) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949); (b) J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 408 (1950).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

TABLE I

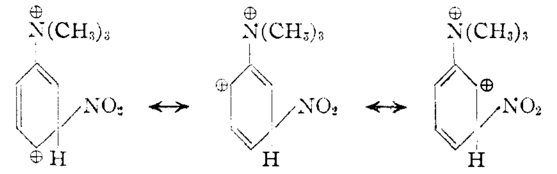
σ-CONSTANTS OF THE $-\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{Cl}$ GROUP

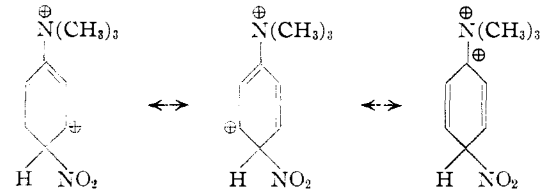
Reaction		Temp., °C.	log $k°$	ρ	log k_{meta}	σ_{meta}	log k_{para}	σ_{para}	$\sigma_{meta} - \sigma_{para}$
Ionization of benzoic acids	50% EtOH	25	-5.71[a]	1.464[a]	-4.22	$+1.02$	-4.42	$+0.88$	$+0.14$
Benzoic acids with diphenyldiazomethane	100% EtOH	30	$+0.041$[a]	0.937[a]	0.893	$+0.91$	0.692	$+0.70$	$+0.21$
Ionization of anilinium ions	H_2O	25	-4.569[b]	2.730[b]	-2.26	+ .85	-2.51	+ .75	+ .10
Ionization of dimethylanilinium ions	H_2O	25	(-4.44)[c]	2.77[c]	-2.60	+ .67	-2.64	+ .65	+ .02
Ultraviolet absorption characteristics[d]	H_2O	..	......	....	.....	....	.....	....	+ .15[e]

[a] Ref. 3a. [b] Ref. 4. [c] Based on values of pK_A of *p*- and *m*-nitrodimethylanilines. [d] L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947). [e] Calculated from λ_{max} of *p*-aminophenyltrimethylammonium chloride (240 mμ) by the procedure of Doub and Vandenbelt.

On the basis of the present results, the inductive effect of a substituent group on an aromatic ring appears to be best regarded as falling off smoothly with distance, possibly in accord with the Coulomb law. Support for this hypothesis is found in the results of an earlier study of the electrical effect of the trimethylsilyl group.[3a,5] The $(CH_3)_3Si-$ group is electron-releasing relative to hydrogen and seems to have no important resonance interaction with the benzene ring.[6] The σ-constants of the group indicate a higher electron density at the meta- than at the para-position as would be expected from an inductive effect which falls off smoothly with distance. This result is significant since none of the usual electrical influences postulated by the English school seems capable of explaining the electrical effect of the $(CH_3)_3Si-$ group.

If the inductive effect of the $-N(CH_3)_3^{\oplus}$ group is admitted to be more powerful at the meta- than at the para-position, a new problem arises in accounting for the very powerful meta-directing influence of the group in electrophilic aromatic substitution reactions.[1] It seems unlikely that resonance such as II can be operative in the transition state of the substitution reaction and thereby favor meta-substitution since this would be evoking resonance as a destabilizing influence. We believe that the simplest explanation is obtained by translation of the ideas of Pfeiffer and Wizinger[7] into the terminology of resonance theory. Using the nitration reaction as an example of a typical electrophilic substitution reaction, we may formulate a transition state having a nitronium ion ($NO_2^{\oplus}$) more or less covalently bonded to the aromatic ring. For meta-substitution, resonance forms such as V can be written for stabilization of the transition state while for para-substitution the corresponding forms VI should be important.


Va Vb Vc


VIa VIb VIc

Consideration of the relative stability of these structures solely on the basis of electrical repulsions between like-charged centers leads to the conclusion that set V is more stable than set VI by some 10 kcal. if each form is assumed to contribute equally.[8] While a calculation of this sort cannot be expected to yield decisive information regarding the actual relative stabilities of the meta- and para-substitution transition states, it seems significant that the electrical repulsions calculated for a simple model are of sufficient magnitude to accommodate easily the observed predominance of meta-substitution.

Experimental

Materials.—*m*-Carboxyphenyltrimethylammonium chloride was obtained as a monohydrate from *m*-benzbetaine[9] by treatment with hydrochloric acid and crystallization from acetone–water, m.p. 181.5–182° (dec.).

Anal. Calcd. for $C_{10}H_{14}NO_2Cl$: C, 55.67; H, 6.54; neut. equiv., 215.7. Calcd. for $C_{10}H_{14}NO_2Cl \cdot H_2O$: C, 51.39; H, 6.90; neut. equiv., 233.7. Found: C, 52.13; H, 6.57; neut. equiv., 231.2.

The material was dried to constant weight in an Aberhalden pistol under reduced pressure and the dried compound had a neutralization equivalent of 216.

p-Carboxyphenyltrimethylammonium chloride was obtained from the corresponding iodide[10] by successive treatments with silver oxide and hydrochloric acid. The product was recrystallized from ethanol and had m.p. 240.4–241.4°.

Anal. Calcd. for $C_{10}H_{14}O_2NCl$: C, 55.67; H, 6.54;

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[5] The interpretation of the work on the trimethylsilyl group[3a] has recently been criticized by A. E. Remick, "Record of Chemical Progress," Kresge-Hooker Scientific Library, Detroit, Mich., Winter 1950 issue, pp. 57–59, who suggested that polarization effects vitiate the comparison between σ-constants obtained from ionization constant and reaction rate measurements of substituted benzoic acids. However, this view cannot be reconciled with the fact that the "polarization effects" seem to occur where least expected, *i.e.*, with meta- rather than para-substituents and not significantly with the usually highly polarizable *p*-amino and *p*-nitro groups. Actually, the only possible interpretation of the anomalies with meta-substituents seems to be on the basis of entropy or proximity effects and it has been noted that the deviations between σ_{meta} values obtained are roughly proportional to the size of the groups involved.

[6] *Cf.* also, the interesting study of H. Gilman and G. E. Dunn, THIS JOURNAL, **72**, 2178 (1950), which presents spectroscopic evidence bearing on this point.

[7] P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928).

[8] In this calculation the C–C bonds of the benzene ring were taken as 1.40 Å. and the C–N distance between C-1 and the $N(CH_3)_3^{\oplus}$ group as 1.50 Å. The dielectric constant was considered to be 2.0.

[9] A. C. Cumming, *Proc. Roy. Soc.* (*London*), **A78**, 108 (1906).

[10] R. Willstätter and W. Kahn, *Ber.*, **37**, 401 (1904).

neut. equiv., 215.7. Found: C, 55.48; H, 6.57; neut. equiv., 216.5.

m-Aminophenyltrimethylammonium chloride was obtained as the hydrochloride from *m*-nitrophenyltrimethylammonium bromide by reduction with hydrogen over platinum in methanol, treatment with silver oxide and acidification with hydrochloric acid. The product was recrystallized from ethanol, m.p. 185–189° (dec.).

Anal. Calcd. for $C_9H_{16}N_2Cl_2$: C, 48.44; H, 7.23. Found: C, 48.19; H, 7.08.

p-Aminophenyltrimethylammonium chloride was obtained as the hydrochloride from *p*-aminophenyltrimethylammonium iodide[11] by successive treatments with an aqueous suspension of lead chloride, hydrogen sulfide to remove excess lead and excess hydrochloric acid. The product was recrystallized from methanol–ether, m.p. 206–206.5° (lit.,[11] 219°).

Anal. Calcd. for $C_9H_{16}N_2Cl_2$: C, 48.44; H, 7.23. Found: C, 48.11; H, 7.00.

m-Dimethylaminophenyltrimethylammonium chloride was obtained as the hydrochloride from *m*-dimethylaminophenyltrimethylammonium iodide[12] by treatment with silver oxide and excess hydrochloric acid. Crystallization from ethanol–acetone yielded hygroscopic material of m.p. 162.6–163.6° (dec.).

Anal. Calcd. for $C_{11}H_{20}N_2Cl_2$: C, 52.59; H, 8.03. Found: C, 52.40; H, 7.95.

m-Dimethylaminophenyltrimethylammonium chloride was similarly prepared except that only the equivalent amount of hydrochloric acid was added. The product was recrystallized several times from chloroform–ethyl acetate and had m.p. 188.7–189.5° (dec.). The substance retained water tenaciously and lost weight only slowly at 100° under reduced pressure. After many hours the m.p. rose to 200.8–202° but the analysis indicates that this material was not completely free of water.

Anal. Calcd. for $C_{11}H_{19}NCl$: C, 61.52; H, 8.92. Found: C, 59.89; H, 9.06.

p-Dimethylaminophenyltrimethylammonium chloride was obtained from the corresponding iodide[13] by successive treatments with an aqueous suspension of lead chloride and hydrogen sulfide to remove the excess lead. The product was recrystallized from methanol–ether, m.p. 261–263° (dec.). The product like the corresponding *m*-compound retained water tenaciously and consequently gave low carbon values on combustion analysis. The material lost water but slowly and the best analysis was obtained only after drying at 110° at 1 mm. for 24 hours.

Anal. Calcd. for $C_{11}H_{19}N_2Cl$: C, 61.52; H, 8.91. Found: C, 59.86, 60.33, 60.83; H, 8.95, 9.01, 8.95.

Ionization Constants.—Apparent ionization constants of *m*- and *p*-carboxyphenyltrimethylammonium chlorides were measured at 25° in 50% water–50% ethyl alcohol (by volume) as described earlier.[3a]

Chloride	Half-point scale reading	Apparent ionization constant $\times 10^6$
m-Carboxyphenyltrimethylammonium	4.22	60.4
p-Carboxyphenyltrimethylammonium	4.42	38.0

Ionization constants (pK_A) of substituted anilinium and dimethylanilinium ions were measured by the procedure of Hammett and Paul[14] as described previously. *m*-Nitroanilinium ion (pK_A 2.62) was used as a standard. The results are given in Tables II and III.

TABLE II

OPTICAL DENSITIES OF COMPLETELY IONIZED AND UNIONIZED SUBSTITUTED ANILINES ($XC_6H_4NR_2$) IN AQUEOUS SOLUTION

X	R	Concn., moles/l. $\times 10^{-5}$	λ, mμ	*D* of unionized form at λ	*D* of ionized form at λ
m-NO_2	H	3.68	225	0.675	0.122
m-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	H	5.52	236	.549	.028
p-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	H	4.41	240	.515	.024
m-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	CH_3	5.04	255	.756	.038
p-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	CH_3	6.59	258	.532	.004

TABLE III

DETERMINATION OF ACIDITY CONSTANTS OF ANILINIUM IONS ($XC_6H_5N^{\oplus}HR_2$)

X	R	*D* at λ	C_X/C	log (C_X/C_{XH})	pK_A
m-NO_2	H	0.376	0.460	−0.071	(2.62)
m-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	H	.372	.660	+ .288	2.26
m-NO_2	H	.366	.441	− .103	(2.62)
p-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	H	.273	.506	+ .011	2.51
m-NO_2	H	.360	.430	− .122	(2.62)
m-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	CH_3	.352	.438	− .109	2.60
p-$N^{\oplus}(CH_3)_3Cl^{\ominus}$	CH_3	.226	.420	− .142	2.64

Rate Runs.—The reaction rates of *m*- and *p*-carboxyphenyltrimethylammonium chlorides with diphenyldiazomethane were measured in absolute ethanol at 30° as described previously.

Chloride	Concn., moles/l.	Half-life, min.	k_2, l./mole-min.
m-Carboxyphenyltrimethylammonium	0.02002	4.39	7.82
p-Carboxyphenyltrimethylammonium	.00599 .00728	24.78 18.50	4.91 (av.)

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[11] J. Pinnow and E. Koch, *Ber.*, **30**, 2860 (1897).

[12] C. Wurster and H. F. Morley, *ibid.*, **12**, 1814 (1879).

[13] C. Wurster, *ibid.*, **12**, 522 (1879).

[14] L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827 (1934); ref. 4, Chap. IX.